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13. ABSTRACT (Maximum 200 words)

A number of experimental studies of the dynamics of bimolecular and unimolecular collisional processes and spectroscopic studies involving molecular free radicals of importance in combustion and atmospheric chemistry have been carried out. These include study of the reaction of Cl atoms with small hydrocarbons, the formation of NCO in the $CN + O_2$ reaction, predissociation of electronically excited NCO, and photodissociation of vibrationally excited halomethanes. The interaction of the HCO radical with Ar was probed through electronic spectroscopy of the weakly bound Ar-HCO complex. A search for the laser fluorescence excitation of the FCO radical was unsuccessful, and bands previously attributed by other workers to this species were definitively assigned to the CH_2CFO radical.

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FINAL REPORT

Paul J. Dagdigian

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I. STATEMENT OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

In this project, we have carried out a number of experimental studies of the dynamics of several bimolecular and unimolecular collisional processes, as well as spectroscopic studies involving molecular free radicals of importance in combustion and atmospheric chemistry. The following subsections describe the specific systems studied and the results obtained.

The Principal Investigator has also written an extensive review[1] of studies, both experimental and theoretical, on collision-induced electronic transitions (including quenching) in diatomic species wherein both the initial and final rovibrational states were resolved. This review highlights examples where the collisional transition is mediated by spectroscopic transitions in the isolated molecule ("gateway" mechanism) or by mixing of the electronic states induced by the approach of the collision partner.

A. Dynamics of Reactions of Cl Atoms with Small Hydrocarbons

We have been investigating the dynamics of photo-initiated abstraction reactions of Cl atoms with small saturated hydrocarbons.[2-4] This class of reactions have been extensively studied in kinetics experiments[5] because of their importance as a temporary sink for chlorine atoms in the atmosphere.[6]

These experiments have been carried out in a recently constructed time-of-flight mass spectrometer (TOFMS).[2] A unique feature of this apparatus is separate pulsed valves for the injection of the Cl photolytic precursor and the hydrocarbon reagent, allowing the study of reactions involving chemically incompatible reagents. The HCl and DCl products were detected state selectively by resonance-enhanced multiphoton ionization (REMPI). The reactions were initiated in crossed, pulsed reagent flows by 355 nm photolysis of Cl_2 to produce the Cl atomic reagents.

We initially studied the reaction of Cl with CH_4, C_3H_8, and $i\text{-}C_4H_{10}$.[2] The Cl + CH_4 reaction is slightly endothermic,

$$Cl + CH_4 \rightarrow HCl + CH_3 , \qquad\qquad \Delta H_0 = +7 \text{ kJ mol}^{-1}, \qquad (1)$$

and only HCl(v=0) products were observed, while v=0 and a small amount of v=1 products were detected for the other reactions. In all cases, only modest rotational excitation appeared in the products, as in the analogous $O(^3P)$ + alkane reactions, which have similar exothermicities but

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higher activation energies and whose dynamics have been extensively studied.[7, 8] Similarly low HCl rotational excitation has been found for the Cl + c-C_6H_{12} and $CH_4(v_3=1)$ reactions.[9-11] The geometry of the Cl + CH_4 transition state was found in *ab initio* calculations[12] to have a linear Cl–H–CH_3 structure. With this geometry, there will be a bias toward linear Cl–H$\cdots$R recoil, and hence little torque will be exerted on the departing HCl product, leading to low rotational excitation, as observed.

The Cl + C_3H_8 and i-C_4H_{10} reactions are complicated by the availability of several reaction pathways, involving the abstraction of primary, secondary, or tertiary hydrogens. We have extended our original experiment[2] to studies with selectively deuterated reagents[3, 4] in order to distinguish these pathways isotopically. The abstraction of primary *vs.* tertiary hydrogens was investigated in the Cl + $(CH_3)_3CD$ reaction.[3] The yield of HCl to DCl product was found to be 3.3 ± 0.4. Hence, this reaction displays a dynamical preference (by a factor of ~ 3 over the ratio of H to D atoms in the hydrocarbon reagent) for the more exothermic pathway, involving abstraction of the tertiary hydrogen. We also studied the Cl + $CD_3CH_2CD_3$ reaction.[4] In this case, the HCl to DCl product branching ratio was found to be 1.1 ± 0.2, again displaying a similar dynamical preference for abstraction of the secondary H atom.

There has been considerable interest in the determination of product c.m. angular distributions and vector correlations for specific internal states through experiments with photo-initiated reactions under bulb conditions. Here, one takes advantage of the anisotropy of the angular distribution of the photolytically prepared reagent to generate an anisotropic distribution of reaction products.[11, 13-15] In our experiments, we have obtained coarse product c.m. angular distributions from the 1-dimensional laboratory velocity distributions derived from the observed HCl^+ time-of-arrival profiles. The derivation of the product c.m. angular distribution is facilitated when the reagent velocities can be neglected.[16] For our original experimental configuration of a 90° intersection angle between the reagent flows, we found from Monte Carlo simulations that the reagent velocities were contributing significantly to the spread in product velocities.[2, 3] In our subsequent experiments, we reduced the intersection angle to 20° and thereby decreased the spread in the reagent relative translational energy distribution and the contribution of the reagent velocities to the width of the product time-of-arrival profiles. From analysis of these profiles for detection of HCl and DCl, we find that for Cl + $(CH_3)_3CD$ the DCl product is mainly backward scattered, while the HCl product is sideways peaked.[3] We believe that the differences in the c.m. angular distribution reflect the different locations of the bonds to be broken on the hydrocarbon relative to

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its center of mass. Similar differences in the c.m. angular distributions of the HCl and DCl products from the Cl + $CD_3CH_2CD_3$ reaction were also found.[4]

In the course of these experiments, we carried out a spectroscopic study of the REMPI spectrum of DCl, in collaboration with R. J. Gordon, his student R. Liyanage, and R. W. Field, and have measured the relative detection efficiency for HCl and DCl.[17] We have also measured transition energies for a number of bands previously observed only in the 1-photon vuv spectrum. In both the HCl and DCl $E-X$ and $F-X$ transitions, the ion signals were found to vary strongly with J', with significant ion fragmentation in the former bands. This variation of REMPI signal strengths was shown to be due to an indirect predissociation, as in the HCl $F-X$ (0,0) band,[18] involving coupling of the bound excited level to a predissociating state.

B. Photodissociation of Vibrationally Excited Halomethanes

There has been considerable interest in exploring the role vibrational energy can play in altering the dynamics of photodissociation.[19] Mode-selective chemistry has been convincingly demonstrated in triatomic systems. Selective modification of the dynamics through vibrational excitation of specific modes should become more difficult in larger molecules. Changes in fragment branching ratios and internal state distributions have been observed in the photodissociation of several 4-atom molecules, including HNCO,[20] C_2HD,[21] and C_2H_2.[22, 23]

It is interesting to investigate the photodissociation of vibrationally excited levels of even larger molecules. We have carried out a study of the photodissociation of C–H stretch overtone excited levels of the atmospherically important halomethanes. For these systems, the coupling of the C–H stretch and CH_3 bending modes in the CH_3X systems[24] might be expected to impede the observation of selectivity in the dissociation dynamics. The specific system we have chosen for initial study is the photolysis of CH_3Cl excited to its fourth C–H stretch overtone level. The first electronic transition in the halomethanes is a $n \rightarrow \sigma^*_{C-Cl}$ transition, and the main photolytic process is cleavage of the C–Cl bond.[25]

In our experiments,[26, 27] we vibrationally excite CH_3Cl by irradiation with near infrared laser radiation and probe the photolytic formation of ground state $Cl(^2P_{3/2})$, spin-orbit excited $Cl(^2P_{1/2})$, and H atoms by REMPI detection in a TOFMS. The same uv laser (~ 240 nm) is used for photolysis and REMPI detection. In contrast to the room-temperature photoacoustic spectrum,[24] which shows only a broad feature for excitation of the fourth C–H overtone, our action spectra for the yields of Cl, Cl*, and H atoms, with our supersonically cooled CH_3Cl

precursor, shows two broad peaks with many narrow features superimposed. On the basis of the vibrational Hamiltonian derived by Duncan and Law,[24] these broad peaks are assigned to excitation of the [5,0,0] and Fermi-resonance coupled [3,0,0] + $4v_2$ levels.

In addition to the formation of Cl atoms, recent experiments by Melchior et al.[27, 28] have shown that formation of H atoms is a minor, but not insignificant (10 – 20 %) channel in the photolysis of HCFC's. This has possible implications for their atmospheric chemistry. We also observe some formation in the photolysis of ground state and vibrationally excited CH_3Cl. Perhaps the most interesting effect of the vibrational excitation is the alteration of the branching ratios for formation of Cl, Cl*, and H atoms. We find that the Cl*/Cl spin-orbit branching ratio is ~ 4 times larger for photolysis of vibrationally excited CH_3Cl than for ground state molecules.[26] On the basis of quantum calculations by Alexander and co-workers[29] of the Cl*/Cl ratio for photolysis of HCl, we believe that a different electronic state is being accessed in the photolysis of vibrationally excited CH_3Cl. By contrast, we observe that the H/[Cl + Cl*] ratio is reduced by a factor of ~ 5 with vibrational excitation of the parent molecule.[27] This result is counter-intuitive since the vibrational energy is initially deposited in the C–H stretch modes, but this may reflect the intramolecular vibrational relaxation (IVR) occurring in the molecule.

C. Formation of NCO in the CN + O_2 Reaction

The CN and NCO radicals are important intermediates in the combustion of nitrogen-containing fuels.[30] The most studied reaction involving these species is the CN + O_2 reaction.[31] The thermal rate constant of this reaction, measured over $13 < T < 4000K$, monotonically increases with decreasing temperature for $T \leq 2000$ K, suggesting that there is no barrier to approach of the reagents. The dominant product channel is formation of NCO + O. Several groups, including our own, have measured the NCO vibronic state distribution.[32-34] In the experiments of Sauder et al.[32] and Phillips et al.,[33] the CN reagent was prepared in a cell by photolysis of a precursor, and the NCO products were detected by laser fluorescence excitation in its $\tilde{A} - \tilde{X}$ band system. In both these experiments, the CN reagent had an approximately room-temperature internal state distribution. A rich NCO spectrum was observed, indicative of considerable vibronic excitation. While unambiguous conversion of fluorescence intensities to populations was not possible because of incomplete information on the band strength factors,[32] it was nevertheless clear that a considerable fraction of the available energy appeared as NCO bending excitation.

In contrast to these cell experiments, the crossed beam experiment of Macdonald et al.[34]

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showed little NCO vibrational excitation. The principal difference is that the CN reagent rotational temperature in the beam experiment is much colder. The differing NCO product state distributions may reflect a strong dependence of the reaction dynamics on the reagent CN rotational excitation. To explore this possibility, we have carried out a new study of the CN + O_2 reaction in a cell, in which the CN reagent was prepared by 193 nm photolysis of BrCN, for which the CN fragment is highly rotationally excited ($E_{rot} \sim 0.7$ eV).[35, 36] Since CN rotational relaxation is occurring as reaction is taking place, we monitored both the CN and NCO product states by laser fluorescence excitation *vs.* photolysis-probe delay. We find that the total concentration of the CN reagent decreases due to reaction at a much slower rate than expected from the 300 K thermal rate constant. This indicates that the reaction cross section for rotationally excited CN reagent is significantly less than for rotationally thermalized CN. The product NCO laser fluorescence spectrum is exceedingly complex. Nevertheless, we were able to show that the rotationally excited CN reagent yields NCO product with greater bending excitation than for thermalized reagent.

D. Predissociation of Electronically Excited NCO

We have also carried out a spectroscopic study of the radiative and nonradiative decay of NCO in both its $\tilde{A}\,^2\Sigma^+$ and $\tilde{B}\,^2\Pi$ electronic states.[37] Most spectroscopic investigations on NCO have centered on its ground $\tilde{X}\,^2\Pi$ electronic state,[38-42] and information about the excited $\tilde{A}$ and $\tilde{B}$ states is more limited. All the vibrational levels of the excited electronic states lie above the lowest $N(^4S)$ + CO dissociation asymptote. Evidence for nonradiative decay of electronically excited NCO was first found by Crosley and co-workers,[43] who observed that the $\tilde{B}(1,0,0)$ decay lifetime was dramatically smaller than for $\tilde{B}(0,0,0)$. Cyr *et al.*[44] carried out a thorough study of the predissociation of $\tilde{B}$ state vibrational levels and observed the opening of the spin-allowed $N(^2D)$ + CO decay channel.

Alexander and Werner[45] have carried out electronic structure calculations to elucidate the mechanism of $\tilde{B}$ state predissociation. They find that this process occurs by an indirect mechanism involving the coupling of the $\tilde{B}$ and $\tilde{A}$ states and the crossing of latter, at a nonlinear geometry, by a repulsive $^4A''$ state correlating with $N(^4S)$ + CO. The crossing of the $\tilde{A}$ and $\tilde{B}$ states occurs near the equilibrium geometry of the latter and provides an explanation for the highly perturbed nature of the $\tilde{B}(0,0,0)$ vibrational level.[46] These *ab initio* calculations suggest that the high vibrational levels of the $\tilde{A}$ state should also be predissociated.

We have carried out our spectroscopic study[37] both to observe $\tilde{A}$ vibrational levels in the

large gap between the highest previously observed[38] level (at 27 701 cm^{-1}) and the $\tilde{B}$ state origin (at 31 751 cm^{-1}) and to determine more precisely the onset of predissociation through measurement of decay lifetimes. For this study, NCO was prepared through the CN + O$_2$ reaction, but with a long photolysis-probe delay to allow for rotational thermalization. We observed and assigned many vibrational levels, principally those with v_3 excitation, in the $\tilde{A}$ state.

The decay lifetimes were found to be approximately constant (*ca.* 280 ns) below 30 000 cm^{-1} excitation energy and then to fall at higher energies, becoming laser pulse width limited by 32 600 cm^{-1}. The lifetimes measured for levels in the energy region around the $\tilde{B}$ state origin were found to be significantly smaller than 280 ns and to vary widely from level to level, reflecting, in part, the varying $\tilde{A}/\tilde{B}$ state mixing. Most of the excited levels were prepared by laser excitation of the ground $\tilde{X}$(0,0,0) level and possessed $^2\Sigma^+$ vibronic symmetry. Excited bend levels of $^2\Pi$ vibronic symmetry were also studied; for these levels the fluorescence appears to break off at an energy < 30 300 cm^{-1}. From the energy dependence of the lifetimes, the onset of predissociation appears to occur at energies just below that of the $\tilde{B}$ state zero-point level. This, as well as the enhanced nonradiative decay for excited bend levels, is consistent with the calculations of Alexander and Werner.[45]

E. Study of the Ar–HCO Interaction through Laser Spectroscopy of van der Waals Complexes

The HCO radical plays in important role in the combustion of hydrocarbons[47] and in atmospheric oxidation.[48] Laser fluorescence excitation in the $\tilde{B}^2A' - \tilde{X}^2A'$ band system[49-52] is particularly convenient for laser diagnostics of HCO in a combustion environment.[53] Meier *et al.*[54] have reported room-temperature quenching cross sections for the HCO $\tilde{B}$(000) vibrational level.

We have carried out a spectroscopic study of the anisotropic interaction of HCO($\tilde{B}$, $\tilde{X}$) with Ar atoms.[55] Ar–HCO van der Waals complexes were prepared in a supersonic jet, through 308 nm photolysis of acetaldehyde in a Ar/He mixture at the orifice of the beam source, and 8 Ar–HCO bands were detected by laser fluorescence excitation. Rotational analysis of some of the bands were carried out, and average Ar–HCO separations (~ 3.7 Å) in both electronic states were determined. Several of the bands were assigned as hot bands ($K'' = 1$) in the ground electronic state. The pattern of bands is the same as for a prolate symmetric top. From the derived A rotational constants, we conclude that the ArCO framework has an approximately T-shaped

geometry in both electronic states. The binding energies in the ground and excited electronic states are quite similar. Our conclusions about the Ar–HCO($\tilde{X}$) potential energy surface (PES) are in agreement with the results of ongoing calculations of this PES by Bowman and co-workers.[56]

With the high signal-to-noise ratio in this study, it was possible to observe transitions in the free H^{13}CO isotopomer. A rotational analysis of the $\tilde{B} - \tilde{X}$ origin band of H^{13}CO was carried out. The isotope shifts of the ν_2' and ν_3' frequencies were measured, and a normal mode analysis for the $\tilde{B}$ state, using the derived H^{13}CO and previously reported[51] frequencies for HCO and DCO, was carried out. Surprisingly, the lowest frequency mode ($\omega_3' = 1107$ cm^{-1}) has mainly CO stretch character, while $\omega_2' = 1412$ cm^{-1} has mainly bending character.

F. Laser Spectroscopy of Oxidized Halon Fragments

We have carried out a study intended to observe the FCO radical by laser fluorescence detection. However, this experiment[57] led to an unanticipated result. The UV absorption spectrum of the FCO radical has been reported both in matrix isolation experiments[58, 59] and through transient absorption in the gas phase.[60, 61] Several long progressions have been observed in the absorption spectrum and have been assigned as transitions to two excited, strongly bent electronic states.[60]

While UV absorption has been employed for FCO kinetic studies,[61] detection by laser fluorescence offers a substantial increase in detection sensitivity. Very recently, Williams and Fleming[62] reported a room-temperature laser fluorescence excitation spectrum assigned to FCO, which was generated in a cell by several different photolytic techniques known to be good sources of this radical, *e.g.* 3-body recombination of F and CO. They investigated the spectral region 29 000 – 32 800 cm^{-1}, which overlaps the lower-energy portion of the FCO absorption spectrum. They find that the absorption and fluorescence excitation spectra are quite different in appearance, and they conclude that different excited electronic states are being accessed. The rotational structure of the bands was found to be very complicated and was not analyzed.

Within the same month, Washida and co-workers[63] reported the identical laser fluorescence spectrum, but generated from the reaction of O(^3P) with halogenated ethylenes (CH$_2$CHF, CH$_2$CF$_2$, and CH$_2$CFCl). With the first reagent, vinoxy (CH$_2$CHO) and a new species could be detected. The latter was also observed in the reactions with the other reagents. Since ethylene reacts with oxygen atoms to form vinoxy in large yield,[64] these authors concluded that the analogous reactions of the halogenated ethylenes would proceed similarly, to yield the CH$_2$CFO

radical, which was assigned as the carrier of the new bands. Quantum chemical calculations were also performed to buttress the vibrational frequency assignments. They also observed the same spectrum upon 193 nm photolysis of acetyl fluoride.

We entered this area of research before knowing of these two studies.[62, 63] We have employed 193 nm photolysis of acetyl fluoride in a supersonic beam in order to carry laser spectroscopic studies of FCO. Slagle and co-workers have employed this as a source of FCO for studies of its thermal unimolecular decomposition through photoionization mass spectrometry.[65] Our jet-cooled spectra show a remarkable reduction in the complexity of the rotational structure of the bands, as compared to room-temperature spectra obtained by Williams and Fleming.[62] We have been able to assign the origin band to an in-plane electronic transition of a near oblate top whose rotational constants are in good agreement with the ground-state equilibrium structure calculated by Furubayashi $et\ al.$[63] We thus confirm the assignment of the spectrum to the $\tilde{B}\,^2A'' - \tilde{X}\,^2A''$ electronic transition of the CH_2CFO radical.

Apparently, the excited states of FCO do not fluoresce to any appreciable extent. It appears that Williams and Fleming observed the strongly fluorescing CH_2CFO radical as an impurity species in their reaction mixtures. The CH_2CFO radical can be formed in our apparatus either by direct C–H bond cleavage in the photolysis of acetyl fluoride or, more likely, through reaction of a small amount of photolytically formed F atoms with the parent molecule. It may be important to study of the kinetics of reactions involving CH_2CFO as this species is readily formed upon oxidation of fluorocarbons.

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